

LIBRATIONS AND VIBRATIONS OF Rb_1C_{60} : POLYMERS AND DIMERS FROM IR AND NEUTRON STUDIES

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Infrared transmission and inelastic neutron scattering measurements were performed in a quest for a further understanding of the inter-fullerene interactions in the monomer, dimer, and polymer structural phases of Rb_1C_{60} . The IR measurements clearly demonstrate the symmetry lowerings due to the bonds between fullerene molecules in the dimer and polymer states. A group theoretical analysis of the activated modes is in good agreement with the structures proposed from x-ray measurements. Elastic neutron scattering structural results show that we are indeed in the dimer or polymer phases, and inelastic scans from -8 to 8 meV transferred energy were performed. The lowest librational mode is seen to be stiffer and less intense in the polymer phase as compared to the dimer, in agreement with a basic picture of the structures.

The A_1C_{60} system, with A=Alkali, is quite a rich system. K_1C_{60} was first found by Winter *et al.*¹ Then after the discovery that Rb_1C_{60} behaved differently when cooled slowly or quickly,³ quite a number of studies were undertaken to elucidate the structural and electronic properties of this material.²⁻⁹ The existence of a phase consisting of linear polymer chains,⁸ which is stable in air^{10,11} has further stimulated interest in these materials. Additionally the rapidly cooled, or quenched, phase was found to form a dimerized structure, the details of which are presented by G. Oszlányi *et al.*¹² The polymer structure has two bonds between each C_{60} molecule while the dimer has one.

In this paper we present infrared (IR) and neutron scattering measurements on phase-pure Rb_1C_{60} powders. For the IR measurements, small amounts of this powder were pressed into KBr pellets inside a glove box. These pellets were then mounted on a HeliTran cryostat and measured by a Bomem MB-155 FTIR spectrometer. Reference scans were obtained on similarly prepared KBr-only pellets. The neutron scattering measurements were performed on approximately 3 grams of Rb_1C_{60} powder sealed with helium in an aluminum can. This can was heated on a hot plate to 450K and then quenched in liquid nitrogen. It was mounted on the cold finger of a large bore "orange" liquid helium cryostat. Measurements were made using the H8 beamline of the High Flux Beam Reactor at Brookhaven National Laboratory, with a pyrolytic

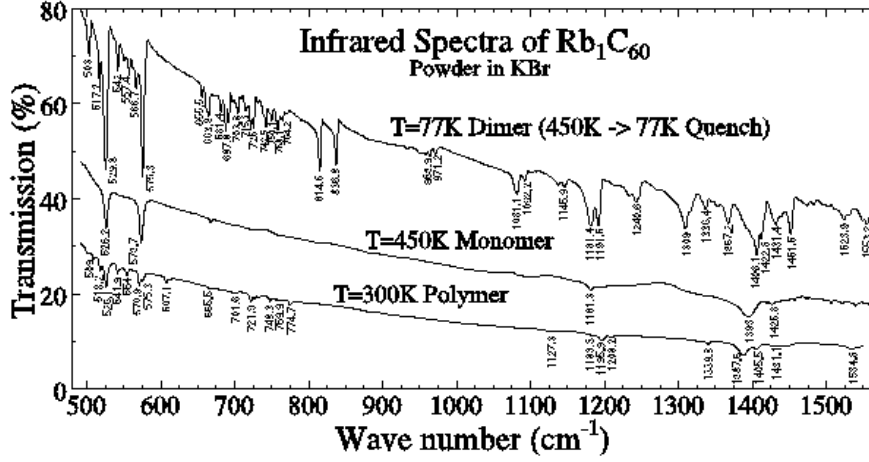


Figure 1: The raw IR transmission spectra of Rb_1C_{60} in all three structural phases. Temperatures are noted and all visible vibrational modes are labeled with their center energy.

graphite monochromator selecting 14.7 meV incident energy neutrons.

The IR results are presented in Figure 1 for all three structural phases. The overall shift of the transmission is an indication of the changing conductivities of the different phases, in agreement with an earlier IR study,⁶ the polymer phase is conducting and the dimerized phase is insulating. In the monomeric phase, only the four group theory allowed F_{1u} derived modes are active. But in the polymer state we see that a number of new modes have become activated. In the dimerized phase even yet modes are readily apparent.

Using group theory to analyze what modes should be visible in the polymer and dimer phases of this material (also see Kamarás *et al.*¹³) we find that the polymer activates the *ungerade* modes of C_{60} while the dimer state activates both the *ungerade* and the *gerade* modes. This is in agreement with the data in Figure 1 in that we see roughly double the number of modes in the dimer spectra as compared to that of the polymer. And if one compares in greater detail⁹ with the well known Raman H_g and A_g modes, we find that indeed we are observing these specific modes in the dimer state and not in the polymer state. It is also interesting to note that the IR spectra of the recently produced $(\text{C}_{59}\text{N})_2$ dimer¹⁴ are quite similar to the dimer spectra presented here.

We performed elastic neutron scattering to confirm that we indeed are in the polymer or dimer states. The data are presented in Figure 2 and are in agreement with previous x-ray results.^{4,8} In particular an arrow above the

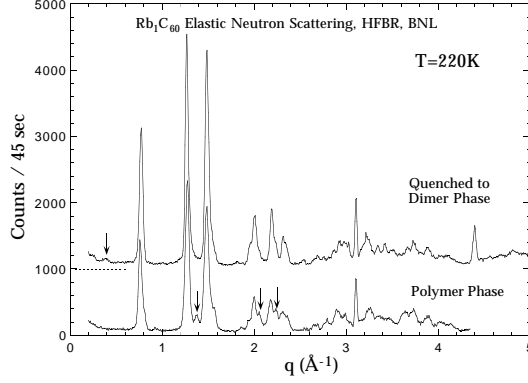


Figure 2: Structural elastic neutron scattering data of Rb_1C_{60} in the dimerized state (upper curve) and polymerized state (lower curve). Upper curve is shifted by 1000 counts for clarity, but is not scaled. Arrows point out some differences between the two states.

dimer data points out were we are seeing a superlattice peak due to the lattice dimerization which has occurred.

Inelastic measurements showing the lowest energy librational mode are shown in Figure 3. The negative energy side corresponds to an energy gain of the neutrons and therefore has a Bose factor associated with it which makes it less intense than the energy loss side. The observed librational mode peaks are well fit by Gaussian line shapes as shown by the solid lines. The peaks are well resolved; our resolution was 0.8 meV while the FWHM of the librations are 3.5 to 4.5 meV.

Two primary difference are evident between the librational modes of the polymer and the dimer structural states. The polymer mode is significantly less intense (a factor of 2) and is stiffer than the dimer mode. The increase in center energy of the mode is expected since a fullerene molecule in the polymer is more rigidly held than in the dimer. And the change in intensity corresponds to a change in the degrees of freedom available to the molecules in each phase. This is also in agreement with the polymerized and dimerized structures^{8,12} as the dimer will have a greater ability to move than that polymer. The energies of these modes is quite close to that of the librational mode in pure C_{60} therefore the underlying interactions may be similar. And if the singly-bonded dimer structure allows for some radial motion of the fullerene around this bond, then the decrease in degrees of freedom may be an indication that the 2 bonds of the polymer are really holding the molecules more rigidly.

Acknowledgments

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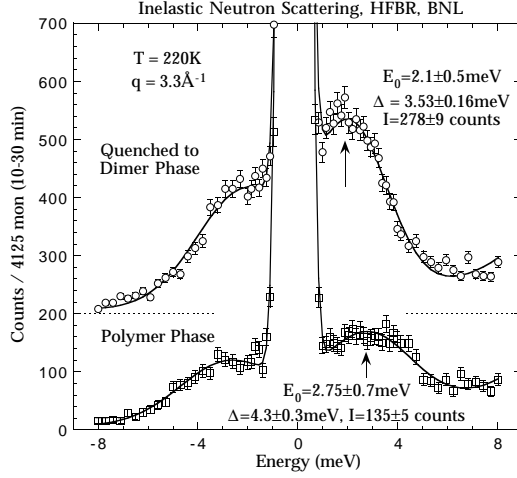


Figure 3: Lowest energy librational mode of Rb_1C_{60} at 220 K in the dimerized state (upper curve) and polymerized state (lower curve). Upper curve is shifted by 200 counts for clarity, but is not scaled. The solid lines are a fit to Gaussian peaks.

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